

# RHENIUM-OXYGEN INTERACTIONS AT HIGH TEMPERATURES

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The reaction of pure rhenium metal with dilute oxygen/argon mixtures was studied from 600° to 1400°C. Temperature, oxygen pressure, and flow rates were systematically varied to determine the rate-controlling steps. At lower temperatures the oxygen/rhenium chemical reaction is rate limiting; at higher temperatures gas-phase diffusion of oxygen through the static boundary layer is rate limiting. At all temperatures post-reaction microstructures indicate preferential attack along certain crystallographic planes and defects.

## 1 Introduction

Rhenium and rhenium alloys have long been favored materials for small thrusters to position satellites. Rhenium has a high melting point, withstands thermal cycling, and is very stable in reducing atmospheres. Like other refractory metals, rhenium readily reacts with oxygen and forms several volatile oxides.

The thermodynamics of these oxides have been studied by several investigators [1-4]. The principal volatile oxides are  $\text{Re}_2\text{O}_7(\text{g})$ ,  $\text{ReO}_3(\text{g})$ , and  $\text{Re}_2\text{O}_6(\text{g})$ . The first oxide has been extensively studied; less is known about the others.

In a gas-solid reaction which generates volatile products, there are three possible rate controlling steps:

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1. Diffusion of the reactant gas, in this case oxygen, through the static boundary layer to the rhenium surface.
2. The chemical reaction at the rhenium/gas interface.
3. Diffusion of the product gases ( $\text{Re}_2\text{O}_7(\text{g})$ ,  $\text{ReO}_3(\text{g})$ , and  $\text{Re}_2\text{O}_6(\text{g})$ ) through the static boundary layer, away from the rhenium surface.

The kinetics of rhenium/oxygen interactions have been studied by several investigators [5-7]. Lavrenko [5] has studied the oxidation of Re from 350-750°C and observed linear reaction rates. Gulbransen *et al* [6] have examined the oxidation of Re in 1-10 torr of flowing oxygen at 600-1400°C. At lower temperatures they found chemical reaction at the surface was rate-controlling and at higher temperature gas-phase transport was rate-controlling.

In this study, the reaction of rhenium with oxygen/argon mixtures is studied from 600-1400°C. Temperature, oxygen partial pressure, and flow rates are systematically varied to determine the rate-controlling step. In addition, post-reaction microstructures are examined to determine the type of attack.

## 2 Experimental

Rolled sheet rhenium (Rhenium Alloys, Elyria, OH) was cut into coupons measuring 1 cm x 1 cm x 0.1 cm. The only detected impurities in this material were 152 ppm Fe and 16 ppm Ti. A series of oxygen (10, 300, 4000 ppm)/argon gas mixtures were prepared as the reactant gas. The samples were suspended from a microbalance (Cahn 1000, Cahn Instrument, Cerritos, CA) into a molybdenum disilicide tube furnace in a standard thermogravimetric apparatus (TGA) configuration. The duration of the exposures ranged from 5-24 hours. Data was continuously collected with a computer. A linear rate constant determined for each condition of temperature, flow rate, and oxygen partial pressure. Experiments were done at 600°, 800°, 1000°, 1200°, and 1400°C at 100 cc/min flow rate. In addition, experiments were done at 200 and 400 cc/min flow rates at 600 and 1000°C. Two or three experiments were done under each condition.

## 3 Results and Discussion

The most useful tool for determining the rate-controlling step is simply the temperature dependence of the overall rate. A gas-phase diffusion controlled process is only weakly temperature dependent; whereas a chemical reaction controlled process shows an exponential dependence on temperature. Figure 1 is a plot of the logarithm of reaction rate vs inverse temperature.

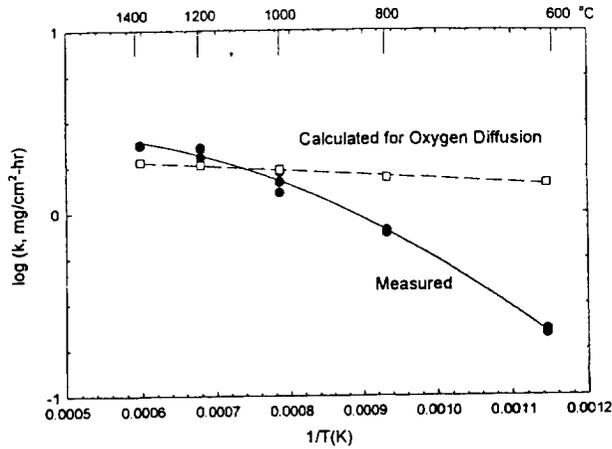


Figure 1. Arrhenius plot of reaction rate vs inverse temperature.

Note that at higher temperatures, the measured rates show only a weak dependence on temperature. This suggests that at 1000, 1200, and 1400°C the rates are controlled by gas-phase diffusion.

At 1000°C, the reaction rate is found to be directly proportional to the partial pressure of oxygen. Further, reaction rate is nearly dependent on flow rate to the 0.5 power. This suggests that oxygen diffusion inward is rate controlling. This can be verified by an estimate of reaction rate for gas-phase diffusion control. An estimate may be done by the following correlation [8]:

$$k = 0.664 (Re)^{0.5} (Sc)^{0.33} \rho(O_2) \frac{D}{L}$$

$$Re = \frac{\rho v L}{\eta} \quad Sc = \frac{\eta}{\rho D}$$

Here Re and Sc are the Reynolds and Schmidt numbers, respectively. In these expressions,  $\rho$  is the density of the O<sub>2</sub>-Ar mixture,  $\rho(O_2)$  is the density of the O<sub>2</sub> reactant,  $v$  is the linear gas velocity,  $\eta$  is the viscosity taken as  $6.16 \times 10^{-4}$  poise,  $L$  is a characteristic dimension taken as 0.5 cm, and  $D$  is the diffusivity of the O<sub>2</sub> reactant. The dashed line in Figure 1 is the results of this calculation. Note the good agreement with the higher temperature data (1000-1400°C). This verifies diffusion of oxygen inward as a rate controlling step.

ref: [8]

At the lower temperatures, another step must be rate controlling. There is a strong dependence of reaction rate on temperature, as shown in Figure 1. Reaction rate is found to be relatively independent of flow rate. Further, reaction kinetics show two regions of linear rates—suggesting different stages of reaction. Thus it is likely that chemical reaction at the rhenium/oxygen interface is rate controlling. The pattern of gas-phase diffusion control at high temperatures and chemical-reaction control at low temperatures has also been observed by Gulbransen, *et al* for Re in reduced oxygen pressure [6] and by Bartlett for tungsten oxidation [9].

After oxidation, the samples showed interesting patterns of attack. Attack was clearly along preferential on certain crystallographic planes.

#### 4 Summary and Conclusions

The oxidation of Rhenium has been studied from 600°-1400°C in dilute oxygen/argon mixtures. Systematic variation of temperature, oxygen pressure, and flow rates indicate gas phase diffusion of oxygen inward is rate-controlling at 1000-1400°C; whereas the chemical reaction of oxygen and Re is rate-controlling at 600 and 800°C.

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